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BATH COMPOSITION FOR ELECTROPLATING TIN-COBALT BINARY ALLOY

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Specification

1. [Title of the invention]

BATH COMPOSITION FOR ELECTROPLATING TIN-COBALT BINARY ALLOY

2. [Scope of the patent claims]

1. (a). As alloy coat forming agent, tin chloride, at least one type of sulfate, and cobalt chloride and at least one type of sulfate

(b). electrically conductive salt

(c). Tartarate or its salt type

Bath composition for electroplating tin-cobalt binary alloy which has the above as the main ingredient

2. (a). As alloy coat forming agent, tin chloride, at least one type of sulfate, and cobalt chloride and at least one type of sulfate

(b). electrically conductive salt

(c). Tartarate or its salt type

(d). glycol ether produced by the reaction of ethylene oxide and alcohol types; it is the bath composition for electroplating tin-cobalt binary alloy which has the above as the main ingredient.

3. [Detailed explanation of the invention]

The present invention relates to the Bath composition for electroplating tin-cobalt binary alloy.

The present invention has a luster, and also, is related to the electroplating bath composition which forms the thick binary

alloy plating coat of tin -cobalt.

The electro deposition method of tin cobalt binary alloy plating coat is well known.

For instance, there are methods described in Electric Chemistry 25, 573, [illeg] 32 by T. L. Ramachar; Tras. Inst. Metal Finishing by R. M. Angleo; Electrodepositing of alloy Vol. 2 by A. Brenner. However, if the coat electrically deposited by the well known methods is used, the defects are that its luster is lost and becomes whitish gray, and when the strong stress is applied, cracking develops.

Because of this, anti corrosion characteristics of these alloy coat is comparable to that of monel metal and inconel, however, its practical usage is nothing more than the thin plating field for decoration.

The inventors herein were involved in researching regarding the plating bath in order to form the plating coat which eliminated the defects of aforementioned plated coat, and filed an application for the patent #136809 in 1975 (Japan Patent Disclosure sho55-18793). According to this, 1-hydroxy ethane -1, 1, phosphoric acid ester is added to electric plating bath, thereby, electroplating coat with a beautiful lust was obtained. However, even in that invention, cracking could not be completely prevented. Hence, in order to improve the aforementioned bath, furthermore, Patent Application Showa52 #55274 (Japan Patent Disclosure

Sh55-17114) was filed. In addition to 1-hydroxy ethane -1, 1, phosphoric acid ester, furthermore, aldehyde type and betain compound were contained in this.

Regarding these baths in actuality used, even in case insoluble anode such as all the carbon and the like or the anode of the same type metal as the alloy coat also, insoluble anode which is actually alkaline bath was used. Using such insoluble anodes and doing electrolysis for a long time, coat forming substance in the bath is consumed and decreased, hence, it was necessary to replenish tin and cobalt separately in this patent application. And it was extremely difficult to control the bath. The present invention relates to the electrically plating bath in which one of aforementioned tin or cobalt which is the alloy coating ingredient can be used as the soluble anode, and bath composition control in electrically plating process is quite easy and binary alloy plating coat formed by electrically plating is superior in outer appearance and physical and chemical characteristics. And, the bath of the present invention can of course use the insoluble anode such as carbon and ferrite and the like.

That is to say, the first invention of this application is that

(a). As alloy coat forming agent, tin chloride, at least one type of sulfate, and cobalt chloride and at least one type of sulfate

(b). electrically conductive salt

(c). Tartarate or its salt type

It is the bath composition for electroplating tin-cobalt binary alloy which has the above as the main ingredient

And the second invention contains (d) glycol ether produced by the reaction of ethylene oxide and alcohol types in the bath of the first invention. In the aforementioned ingredient (a) is an electrically plating coating forming agent, and is used in the form of each chloride of tin cobalt or its sulfate or mixture. (b) is necessary for electrically plating operation, and well known ones are electric conductivity salt, for instance, potassium chloride, sodium chloride, ammonium chloride, potassium sulfate, ammonium sulfate and the like are used. (c) Tartarate such as tartaric acid, potassium Tartarate, soda Tartarate, ammonium Tartarate and the like are used. The purpose to add (c) is to polarize so that electrical potential of the deposition of two types or more of the metal are matched in number or approached.

(d) provides the luster on the electrically plating coat formed, for instance, locally sold Glyco solve which is the product name by Mitsui Toatsu Co., such as ethylene glycol mono methyl ether, ethylene glycol mono isopropyl ether, diethylene glycol mono methyl ether, diethylene glycol mono isopropyl ether, ethylene glycol mono methyl ether acetate, ethylene glycol mono isopropyl ether acetate and the like are used. Regarding the substance listed in (b), (c) and (d), even one type shows additive effects, and

however, it can be two types or more.

Next, the preferred amount in bath composition of this substance will be explained.

As alloy coat forming agent, its entire amount or as the metal elements, the range of tin 1.6g/liter~102g/liter, cobalt 2.1g/l~62.0g/l is suitable in practicality. If the density is too high, the plating solution becomes too viscous, thus workability is lost. If the density is too small, current efficiency decreases, it takes time to obtain a coat with a fixed thickness, thus reducing the workability consequently.

As the electric conductivity salt, 50g/liter~300g/liter range is good, and if this range is exceeded, streaks are produced on the coat, causing defective plating, and if it does not attain this range, resistance in the bath increases, thus joule heat is generated, which is not preferred, and current efficiency is reduced.

Regarding tartaric acid or its salt types, the range is 50g/liter ~ 200 g/liter, and when this range is exceeded, streaks are generated on the plated coat, and it becomes the cause of generating pits on the plating coat, which is not preferred.

And if this ranged is not arrived at, eutectoid phenomenon is not recognized, the corrosion characteristics of the deposited plated coat are greatly decreased, the purpose to obtain alloy coat can not be attained.

Regarding glycol ether type, its range is 1g/liter~20g/l, and if it is smaller than this, additive effect is not clear, and if this is exceeded, plated coat produces whitish turbidity, which does not match the original purpose.

By using the electroplating bath composition of this invention, the condition to engage in plating operation is that bath temperature is 40 ~ 70 deg C, cathode current density is 0.2A/dm² ~2A/dm², pH 0~4.0.

And as anode, soluble anode, that is, tin, cobalt can be used which is the coat forming substance in acid bath also. And, for instance, in case tin is used for anode in acid bath in order to form tin cobalt alloy coat, tin melts into the bath, hence, as the plating progresses, alloy coat forming agent to be replenished naturally becomes only cobalt. Hence, the bath composition control becomes quite easy.

Next, the reason for condition restriction will be described next.

Regarding bath [illeg], in case it does not reach 40 deg C, bath resistance decreases rapidly, electric deposition speed slows down, thus losing productivity greatly. And, if it exceeds 70 deg C or more, it becomes difficult to use the tank made of vinyl chloride and liquid evaporates a lot, and unnecessary amount of energy is consumed, which is not preferred. When the cathode current density exceeds 2A/dm², partial burnt deposit is produced

and in case it does not reach 0.2A/dm², it gets whitish turbid partially.

Next, the present invention will be explained regarding embodied examples and comparison examples.

Embodied examples 1~6, comparison examples 1~2 (used cobalt soluble anode)

Table 1 shows bath composition and table 2 shows electrolysis condition. And all the compositions are expressed by g/l (liter)

See the original table for better reading of compounds

	Embodied examples						Comparison examples	
Compound	1	2	3	4	5	6	1	2
SnCl ₄ · 5H ₂ O	200	100	50	30	30	20	100	30
CoCl ₂ · 6H ₂ O	100	50	30	15	10	8	50	10
KCl	300					30		
NH ₂ Cl		200		70	70		200	70
NaCl			150					
K ₂ O ₄ H ₂ O ₂	200	180			40			
Na ₂ C ₄ H ₄ O ₂			120					
(NH ₄) ₂ C ₂ H ₄ O ₂				50		15		

Table 2

Anode: cobalt

Anode current density: 0.2~0.5A/dm²

Cathode current density: 1~2A/dm²

Bath temperature: 40~50 deg C

pH: 1.5~3.0

Result: in embodied example 1~6, metal ratio tin 82~89 weight

%, cobalt 18~17 weight %, thus silver colored alloy coat was obtained which shows a strong resistance against thick nitric acid and superior in anti corrosion characteristics. It did not show any change in 72 hours of salt water spraying test and outdoor exposure for 50 days and it was good in finger printing resistance characteristics by JISZ 2731. According to pin hole testing for 30 minutes at 150 deg C and heat cycle test for 30 minutes at the normal temperature by JIS-H8612, JIS-H-8613, it did not change, and according to the bending test by JIS-H-8672, it did not peel.

And cobalt in anode dissolves in bath, liquid replenishment can be done using $\text{SnO}_2 \cdot 4\text{H}_2\text{O}$ mainly, the electrically plating operation was easy.

Regarding all of the comparison examples, electric deposition had excess tin, there was no nitric acid resistance, and it was quite unsatisfactory compared with the regular alloy composition.

Embodied examples 7~12, comparison examples 3~4 (used tin soluble anode).

Table 3 shows bath composition and table 4 shows electrolysis condition.

Table 3.

Compound	Embodied example						Comparison example	
	7	8	9	10	11	12	3	4
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	250	200	100	50	30	20	200	20

SnCl ₂ ·2H ₂ O	100	170	70	15	8	5	170	5
KCl		200				30	200	30
NH ₄ Cl	300			80	80			
NaCl			160					
K ₂ O ₄ H ₄ O ₂			160					
Na ₂ C ₄ H ₄ O ₄	100		120					
(NH ₄) ₂ C ₄ H ₄ O ₂		140		100				

Table 4

Anode: tin

Anode current density: 0.2~0.5A/dm²

Cathode current density: 1~2A/dm²

Bath temperature: 40~55 deg C

pH: 3.0~5.0

Result: in embodied example 7~12, metal ratio tin 82 weight %, cobalt 18 weight %, and in all points, same good binary alloy coat as the embodied example 1~6 was obtained.

And, since tin in anode dissolves into the bath, liquid replenishment can be done using CoCl₂·6H₂O mainly, the electrically plating operation was easy.

Regarding all of the Comparison examples, electric deposition had excess cobalt coat, there was no nitric acid resistance, and it was quite unsatisfactory compared with the regular alloy composition.

Embodied examples 13~17, comparison examples 5~7 (used cobalt anode).

Table 5 shows bath composition and table 6 shows electrolysis

condition.

Table 5.

	Embodied example					Comparison example		
Compound	13	14	15	16	17	5	6	7
SnSO ₄ ·2H ₂ O	150	100	90	40	20	100	40	20
CoSO ₄ ·7H ₂ O	70	65	50	21	10	65	21	10
K ₂ SO ₄				80	50		80	50
(NH ₄) ₂ SO ₄	200	150	100			150		
K ₂ C ₄ H ₄ O ₂		50		40				
Na ₂ C ₄ H ₂ O ₂			50		40			
(NH ₄) ₂ C ₄ H ₄ O ₄	80							

Table 6

Anode: cobalt

Anode current density: 0.2~0.5A/dm²

Cathode current density: 1~2A/dm²

Bath temperature: 40~50 deg C

pH: 1.5~3.0

Result: in embodied example 13~17, metal ratio tin 82~83 weight %, cobalt 18~17 weight %, and in all points, same good binary alloy coat as the embodied example 1~6 was obtained.

And, since tin in anode dissolves into the bath, liquid replenishment can be done using SnSo₄·2H₂O mainly, the electrically plating operation was easy.

Regarding all of the Comparison examples 5~7, all of them were quite a bit inferior to the regular alloy composition.

Embodied examples 18~22, comparison examples 8~10 (used tin anode).

Table 7 shows bath composition and table 8 shows electrolysis condition.

Table 7.

	Embodied example					Comparison example		
Compound	18	19	20	21	22	8	9	10
CoSO ₄ .7H ₂ O	200	150	100	80	40	150	80	40
SnSO ₄ . 2H ₂ O	90	52	35	25	15	52	35	25
K ₂ SO ₄				80	50		80	50
(NH ₄) ₂ SO ₄	200	150	100			150		
K ₂ C ₄ H ₄ O ₂			80		50			
Na ₂ C ₄ H ₄ O ₂		70		60				
(NH ₄) ₂ C ₄ H ₄ O ₂	100							

Table 8

Anode: tin

Anode current density: 0.2~0.5A/dm²

Cathode current density: 1~2A/dm²

Bath temperature: 40~55 deg C

pH: 3.0~5.0

Result: in embodied example 18~22, metal ratio tin 82~83 weight %, cobalt 18~17 weight %, and in all points, same good binary alloy coat as the embodied example 1~6 was obtained.

And, since tin in anode dissolves into the bath, new liquid replenishment can be done using CoSO₄.7H₂O mainly.

Regarding all of the Comparison examples, all of them were quite a bit inferior to the regular alloy composition and was unsatisfactory.

Embodied examples 23~34, comparison examples 11~14 (used insoluble

anode).

Table 9 shows bath composition and table 10 shows electrolysis condition.

Table 9.

*1: chloride bath, *2: sulfate bath

	Embodied example							
	23	24	25	26	27	28	29	30
Electrode	Carbon	Carbon	Carbon	Carbon	Carbon	Carbon	Ferrite	Ferrite
Bath type	*1	*1	*1	*1	*1	*1	*2	*2
SnO12.5H2o	100	50	20					
SnCl2.2H2O				80	60	20		
CnCl2.8H2o	40	30	8	160	130	50		
Sn(SO4)2							100	40
SnSO4.2H2O								
CoSO4.7H2O							60	20
KCl		70		100		80		
K2SO4								80
NH4Cl	200		50		90			
(NH4)2 SO4								150
K2O2H4O4	100	80	70	120	90	80	60	40

	Embodied example				Comparison example			
	31	32	33	34	11	12	13	14
Electrode	Ferrite	Ferrite	Ferrite	Ferrite	Carbon	Carbon	ferrite	ferrite
Bath type	*2	*2	*2	*2	*3	*3	*3	*3
SnO12.5H2o					100			
SnCl2.2H2O						60		
CnCl2.8H2o						40	130	
Sn(SO4)2	30							100
SnSO4.2H2O		100	50	20			100	
CoSO4.7H2O	10	210	110	50			210	60
KCl								

K ₂ SO ₄		100					100	
NH ₄ Cl					200	90		150
(NH ₄) ₂ SO ₄	100		100	70				
K ₂ C ₂ H ₄ O ₄	40	80	70	70				

Table 10

Anode current density: 0.2~0.5A/dm²

Cathode current density: 1~2A/dm²

Bath temperature: 50 deg C

Result: the alloy coat with somewhat similar characteristics as the embodied example 1~6 was obtained. And regarding comparison example 11~14, similar results as in each comparison example 1~2, 3~4, 5~7 and 8~10 were obtained.

Regarding Embodied example 1~34, all chloride bath or sulfate bath were single. Next mixed bath embodied example will be shown.

Embodied examples 35~44

In table 11 is shown bath composition and anode type and table 12 described the electrolysis condition.

Table 11

	Embodied example							
	35	36	37	38	39	40	41	42
Electrode	Cobalt	Cobalt	Cobalt	Cobalt	Tin	Tin	Tin	Tin
SnO ₁₂ .2H ₂ O			50			40		30
SnCl ₄ .5H ₂ O	200						100	
SnSO ₄ .2H ₂ O		200			200			
Sn(SO ₄) ₂				100				
CoCl ₂ .6H ₂ O		100		40	80			120

CoSO ₄ ·7H ₂ O	50		120			150	100	
KCl	250					100		
K ₂ SO ₄		150						
NH ₄ Cl			100		100		100	100
(NH ₄) ₂ SO ₄				120				
K ₂ C ₄ H ₄ O ₄	200	200	200	200	200	200	150	100

	Embodied example		Comparison example				
	43	44	15	16	17	18	19
Electrode	Carbon	Ferrite	Cobalt	Cobalt	Tin	Tin	Ferrite
SnO ₁₂ ·2H ₂ O	150				40		
SnCl ₄ ·5H ₂ O			200			100	
SnSO ₄ ·2H ₂ O		200		200			200
Sn(SO ₄) ₂							
CoCl ₂ ·6H ₂ O		80		80			80
CoSO ₄ ·7H ₂ O	300		50		150	100	
KCl			250		100		
K ₂ SO ₄							
NH ₄ Cl	100	100		100		100	100
(NH ₄) ₂ SO ₄							
K ₂ C ₄ H ₄ O ₄	100	100					

Table 12

Anode current density: 0.2~0.5A/dm²

Cathode current density: 1~2A/dm²

Bath temperature: 55 deg C

pH: 1.5~4.0

Result: regarding embodied examples 35~44, similar result as in the embodied examples 1~6 were obtained.

Regarding comparison examples 15~19. Partially, sponge like deposition was obtained, which is useless as plating coat.

Next, embodied example will be described in which glycol ether produced by reacting ethylene oxide and alcohol type was sulferized.

Embodied examples 45~52

Alcohol ether type shown next is added to the optionally selected composition from the compositions in the aforementioned embodied examples, and electrically plated. Then, luster increase condition was studied.

As to glycol ether, the product name Glycosolb made by Mitsui Toatsu was used.

(a). CH ₂ O. C ₂ H ₄ OH	Glycosolb M	Ethylene glycol mono methyl ether
(b) CH ₂ >Ch.O.C ₂ H ₄ OH CH ₂	Glycosolb IP	Ethylene glycol mono isopropyl ether
(c) CH ₂ .O.O ₂ H ₄ O.C ₂ H ₄ OH	Glycosolb DM	Diethylene glycol mono methyl ether
(d) OH ₂ > CH.O.O ₂ H ₄ O-C ₂ H ₄ .OH OH ₂	Glycosolb DIP	Diethylene glycol mono isopropyl ether
(e)	Glycosolb TIP	
(f) CH ₄ .O.C ₂ H ₄ -O-OOCH ₂	Glycosolb MGA	Ethylene glycol monomethyl ether acetate
(g) CH ₂ > CHO.C ₂ H ₄ O.COOH ₃ CH ₃	Glycosolb IPCA	Ethylene glycol monoisopropyl ether acetate

As to the additive amount of glycol ether, vis-à-vis bath in relation to (1) ~ (3), it is 5~10ml per liter, and in relation to (4) ~ (7), 1~5ml is added, thus executing the electrically

plating. Electrolysis condition is the same as the case in which glycol ether is not added.

Table 13 shows its result.

In the table, "S" is when the luster increase effect is slight; "T" is when the lust increase result is somewhat better than "S". "C" is when luster increase is great

Table 13

*1: embodied example which corresponds to the composition before adding

Embodied example	Additive type *1	1	2	3	4	5	6	7
45	Embodied example 5	S	T	C	C	C	C	T
46	Embodied example 11	T	C	C	C	C	C	T
47	Embodied example 16	T	C	C	C	C	C	C
48	Embodied example 21	T	C	C	C	C	C	C
49	Embodied example 24	T	C	C	C	C	C	S
50	Embodied example 26	T	C	C	C	C	T	S
51	Embodied example 30	C	C	C	C	C	C	C
52	Embodied example 33	C	C	C	C	C	C	C

As described above, it shows that by adding glycol ether, the coat luster improves. As shown above, the bath of the present invention enables the electrically plating using soluble or insoluble anodes, and the formed tin cobalt coat has a great acid resistance characteristics. That is, the bath of the present invention has a high practical application value.